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| (54) Title: COMPOSITIONS COMPRISING HYDROPHILIC SILICA PARTICULATES (57) Abstract <p>The present invention relates to structured surfactant compositions comprising a detergent surfactant and hydrophilic silica particulates to be used in granular detergent compositions. The preferred silica particulate is hydrophilic precipitated silica. The process for making a structured surfactant composition comprising a detergent surfactant and hydrophilic silica particulates is also included. The present invention encompasses a structured surfactant composition consisting essentially of: (a) from about 35 % to about 60 % of a detergent surfactant; (b) from about 1 % to about 20 % of hydrophylic, finely-divided silica particulate; and (c) from about 15 % to about 25 % moisture.</p> | | |

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COMPOSITIONS COMPRISING HYDROPHILIC SILICA PARTICULATES

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FIELD OF THE INVENTION

The present invention relates to structured surfactant compositions comprising a detergent surfactant and hydrophilic silica particulates to be used in granular detergent compositions. The preferred silica particulate is hydrophilic precipitated silica. The process for making a structured surfactant composition comprising a detergent surfactant and hydrophilic silica particulates is also included.

15

BACKGROUND OF THE INVENTION

It is desired to increase the active level of detergent surfactants in compositions comprising said surfactants in order to facilitate the manufacture of detergent compositions containing high active levels. In addition, it is also desirable to have surfactant compositions that are pumpable and generally easy to transport and transfer from one manufacturing location to a granulation site. One way to meet these needs is by mixing a chemical structuring agent to the detergent surfactant. Prior art includes EPO 508 543 published October 14, 1992 and U.S. 4,925,585 granted May 15, 1990.

It has now been found that incorporating hydrophilic, finely-divided silica particulates as a highly-preferred structuring agent with detergent surfactant enables the formation of structured surfactant compositions which have high levels of active. Preferably, the detergent surfactant is in an aqueous paste form. Structuring of the paste means the addition of a chemical in a solid, liquid, or solution form to change the structure of the paste or modify its physical characteristics to facilitate the manufacture of high active detergent agglomerates which otherwise are not easily obtainable under normal operating conditions. In addition, when such structured surfactant compositions are mixed with other detergent adjuvants such as additional surfactants, detergent builders, inorganic salts, silica, and mixtures thereof to form granular detergent compositions, such granules are free flowing and easy to transport and transfer.

SUMMARY OF THE INVENTION

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The invention encompasses a structured surfactant composition consisting essentially of:

- (a) from about 35% to about 60% of a detergent surfactant;
- (b) from about 1% to about 20% of hydrophilic, finely-divided silica particulate; and
- (c) from about 15% to about 25% moisture.

The invention further encompasses a granular detergent composition comprising:

- 5 (a) from about 2% to about 70% of a structured surfactant composition, the surfactant composition consisting essentially of:
- (i) from about 35% to about 60% of a detergent surfactant;
- (ii) from about 1% to about 20% of hydrophilic, finely-divided silica particulate; and
- (iii) from about 15% to about 25% moisture; and
- 10 (b) from about 30% to about 98% other detergent adjuvants selected from the group consisting of other detergent surfactants, detergent builders, silica, and mixtures thereof.

A process for making structured surfactant compositions is also included.

15 All documents referenced herein are incorporated by reference.

DETAILED DESCRIPTION OF THE INVENTION

20 This invention relates to compositions with a detergent surfactant and hydrophilic, finely-divided silica particulate.

Ingredients, as well as optional ingredients, as well as the process for making a granular detergent composition or an additive composition for a detergent composition are described in detail hereinafter.

25 Structured Surfactant Composition

The structured surfactant composition of the present invention comprises by weight:

- (a) from about 35% to about 60%, preferably from about 35% to about 50%, most preferably from about 40% to about 45% of a detergent surfactant;
- 30 (b) from about 1% to about 20%, preferably from about 1% to about 10%, most preferably from about 2% to about 5%, of hydrophilic, finely-divided silica particulate; and
- (c) from about 15% to about 25% moisture, wherein the ratio of the silica particulate to moisture is from about 1 : 5 to about 1 : 25, more preferably from about 1 : 5 to about 1 : 7.5.

35 The structured surfactant composition can be mixed with other detergent ingredients to form detergent compositions. If the structured surfactant is directly made into a detergent composition, the detergent composition would comprise from about 20% to about 65%, preferably from about 30% to

about 65%, most preferably from about 45% to about 65% structured surfactant composition. The granular detergent composition preferably has a particle size of a maximum of 5% on 14 Tyler mesh.

The particulate silica is added to the surfactant paste, which typically contains 15% to about 25% moisture, as well as salts which are the by-product of neutralization. The particulate silica
5 absorbs the water and a hardened continuous paste is formed. When shear force is applied to the hardened paste, the paste becomes a flowable liquid, which is easily dispersed into fine droplets by using any conventional high-shear agglomerating mixer. The droplets are added with other powder ingredients to form individual particles with have a particle size of a maximum of 5% on 14 Tyler mesh and a minimum of 5% through 100 Tyler mesh. The droplets form particles inside a typical
10 agglomerating mixer. These droplets once formed into a particle, do not re-form a continuous hardened paste. This results in the formation of particle agglomerates to the specific particle size distribution that is required to maintain solubility, handling, etc.

Detergent Surfactant

15 The detergent surfactant is any surfactant selected from the group of consisting of anionics, zwitterionics, ampholytics, cationics, and mixtures thereof. Preferably, the detergent surfactant is anionic surfactant. Most preferably, the detergent surfactant is ethoxylated anionic surfactant.

The anionic surfactant can be selected from:

- 20 (a) linear or branched chain alkyl benzene sulfonate having an C8-20 alkyl chain, preferably C10-18 alkyl chain, and most preferably a C12-16 alkyl chain;
- (b) alkyl sulfate having a C8-20 alkyl chain, preferably C14-18 alkyl chain, most preferably C12-16 alkyl chain;
- (c) mixtures thereof.

25

Preferred is Alkylalkoxy sulfate comprising an alkyl portion of from 6 to 18 carbon atoms and an alkoxy portion comprising, an average, from about 0.5 to about 20 moles of alkoxy, preferably ethoxy, units, more preferably from about 0.5 to about 5 ethoxy units.

30 An anionic surfactant that is most preferable is the alkyl ether sulfate of the formula $R-E_nSO_3M$, wherein:

- (i) R is C8-20; and preferably, C12-15, alkyl chain (mixed chain);
- (ii) E is an ethoxy unit;
- (iii) n is from 1-20; preferably, n=3; and
- 35 (iv) M is a suitable cation, preferably sodium ion.

Useful anionic surfactants include water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Water-soluble salts of the higher fatty acids, i.e., "soaps", also are useful anionic surfactants herein. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Examples of soaps are the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soaps.

Other anionic surfactants useful herein include:

Sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil;

Sodium coconut oil fatty acid monoglyceride sulfonates and sulfates;

Sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates, and sodium or potassium salts of methyl ester $R-CH(SO_3M)-COOR'$, wherein R is C₈-C₂₂ alkyl or alkenyl, R' is C₁-C₄ alkyl, and M is a counter ion, preferably Na or K, such as disclosed in WO-93-05013, published March 18, 1992; sulfonates;

Alpha-sulfonated fatty acid alkyl ether surfactant of the formula $R'-C(SO_3)H-C(O)-OR''$, wherein R' is C₈-20; most preferably C₈-18, alkyl chain; and R'' is C₁-C₄ alkyl, preferably methyl;

Secondary alkyl sulfates having an alkyl chain of from 10 to 20 carbon atoms; and

Alkyl ethoxy carboxylates of the formula $RO(CH_2CH_2O)_xCH_2COO^-M^+$, wherein R is a C₆ to C₁₈ alkyl; x ranges from 0 to 10, and the ethoxylate distribution is such that on a weight basis, the amount of material where x is 0 is less than 20%, the amount of material where x is greater than 7 is less than 25%, and wherein the average x is 2-4 when the average R is C₁₃ or less, and is 3-6 when R is greater than C₁₃; and M is an alkali metal, alkali earth metal, ammonium, mono-, di-, and tri-ethanol ammonium.

One or various aqueous pastes of the salts of anionic surfactants is preferred for use in the present invention. It is preferred that the moisture in the surfactant aqueous paste is as low as possible, while maintaining paste fluidity, and minimizing the amount of free water that may need to be removed, by drying for example, since low moisture leads to a higher concentration of the surfactant in the finished particle. Preferably the paste contains from about 10% to about 40% water, more preferably from about 15% to about 30% water, and most preferably from about 20% to about 30% water.

The activity of the surfactant paste is at least 30% and can go up to about 90%; preferred activities are: 70-80%.

Cationic surfactants can also be used as a detergent surfactant herein and suitable quaternary ammonium surfactants are selected from mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Ampholytic surfactants can also be used as a detergent surfactant herein, which include aliphatic derivatives of heterocyclic secondary and tertiary amines; zwitterionic surfactants which include derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds; water-soluble salts of esters of alpha-sulfonated fatty acids; alkyl ether sulfates; water-soluble salts of olefin sulfonates; beta-alkyloxy alkane sulfonates; betaines having the formula $R(R^1)_2N^+R^2COO^-$, wherein R is a C₆-C₁₈ hydrocarbyl group, preferably a C₁₀-C₁₆ alkyl group or C₁₀-C₁₆ acylamido alkyl group, each R¹ is typically C₁-C₃ alkyl, preferably methyl and R₂ is a C₁-C₅ hydrocarbyl group, preferably a C₁-C₃ alkylene group, more preferably a C₁-C₂ alkylene group. Examples of suitable betaines include coconut acylamidopropyldimethyl betaine; hexadecyl dimethyl betaine; C₁₂₋₁₄ acylamidopropylbetaine; C₈₋₁₄ acylamidohexyldiethyl betaine; 4[C₁₄₋₁₆ acylmethyldimethyldiethylammonio]-1-carboxybutane; C₁₆₋₁₈ acylamidodimethylbetaine; C₁₂₋₁₆ acylamidopentanedimethylbetaine; and [C₁₂₋₁₆ acylmethyldimethyldiethylbetaine. Preferred betaines are C₁₂₋₁₈ dimethyl-ammonio hexanoate and the C₁₀₋₁₈ acylamidopropane (or ethane) dimethyl (or diethyl) betaines; and the sultaines having the formula $(R(R^1)_2N^+R^2SO_3^-)$ wherein R is a C₆-C₁₈ hydrocarbyl group, preferably a C₁₀-C₁₆ alkyl group, more preferably a C₁₂-C₁₃ alkyl group, each R¹ is typically C₁-C₃ alkyl, preferably methyl, and R² is a C₁-C₆ hydrocarbyl group, preferably a C₁-C₃ alkylene or, preferably, hydroxyalkylene group. Examples of suitable sultaines include C₁₂-C₁₄ dimethylammonio-2-hydroxypropyl sulfonate, C₁₂-C₁₄ amido propyl ammonio-2-hydroxypropyl sultaine, C₁₂-C₁₄ dihydroxyethylammonio propane sulfonate, and C₁₆₋₁₈ dimethylammonio hexane sulfonate, with C₁₂₋₁₄ amido propyl ammonio-2-hydroxypropyl sultaine being preferred.

Hydrophilic Silica Particulates

The structured surfactant compositions of the present invention contains, in addition to a
5 detergent surfactant, from about 0.2% to about 20%, preferably from about 1% to about 10%, most
preferably from about 2% to about 5%, of hydrophilic, finely-divided silica particulate. Preferably,
the particulate is a hydrophilic precipitated silica. Such materials are extremely fine-particle size
silicon dioxides. Its surface area ranges preferably from 140 to 550 m²/g as measured by the BET
nitrogen adsorption method. The surface of the silica has both internal and external surface area which
10 allows for the easy absorption of liquids. Dibutyl Phthlate absorption is the method used to determine
the absorptive capability of preprecipitated silica. Generally, a precipitated silica can adsorb 2 to 3 times
its weight.

Precipitated silica materials usually appear in the form of agglomerates. The average
agglomerate size of the silica range from about 50 to 100 microns. The silica agglomerates may be
15 milled by various known methods to reduce the agglomerate size to the range of 2 to 15 microns. The
pH of the silica is normally from about 5.5 to about 7.0.

The hydrophilic silica can also be a fumed silica. Hydrophilic precipitated silica materials
useful herein are commercially available from Degussa Corporation under the names SIPERNAT 22S,
22LS, 50S.

20

Detergent Adjuvants

Preferably, the detergent adjuvants are from about 35% to about 99% of the detergent
composition. The compositions herein can optionally include one or more other detergent adjunct
25 materials or other materials for assisting or enhancing cleaning performance, treatment of the substrate
to be cleaned, or to modify the aesthetics of the detergent composition (e.g., perfumes, colorants, dyes,
etc.). The following are illustrative examples of such adjunct materials.

Other detergent surfactants include surfactants described above. In addition, a hydrotrope,
30 or mixture of hydrotropes, can be present in the laundry detergent bar. Preferred hydrotropes
include the alkali metal, preferably sodium, salts of toluene sulfonate, xylene sulfonate, cumene
sulfonate, sulfosuccinate, and mixtures thereof. Preferably, the hydrotrope, in either the acid form
or the salt form, and being substantially anhydrous, is added to the linear alkyl benzene sulfonic acid
prior to its neutralization. The hydrotrope will preferably be present at from about 0.5% to about
35 5% of the laundry detergent bar.

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

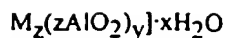
The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the triphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

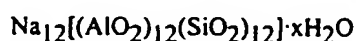
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in

granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued
5 January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application
10 86200690.5/0.200.263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the
15 compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-
20 known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Hydrophilic silica particulates as described above is a preferred detergent adjuvant.

25

Other Adjunct Ingredients

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group
30 consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates,
35 N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

5 Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and
10 Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

15 Clay Soil Removal/Anti-redeposition Agents - The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

20 The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylene-pentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be
25 used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred
30 antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of
35 zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance

overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing
5 suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric
10 segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to
15 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the
20 dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-
25 soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the
30 maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably
35 from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

- 5 Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles,
10 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

- Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners
15 include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis- (1,2,3-triazol-2-yl)-stil- benes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin;
20 1,2-bis(-venzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naph-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton. Anionic brighteners are preferred herein.

- Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated
25 into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

- A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical
30 Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali
35 metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g.,

fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlorotriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 50°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of (CH₃)₃SiO_{1/2} units of SiO₂ units in a ratio of from (CH₃)₃SiO_{1/2} units and to SiO₂ units of from about 0.6:1 to about 1.2:1; and

(iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is
5 branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a
10 polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in
15 granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991, 5,288,431, Huber et al., issued February 22, 1994, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of
20 less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and
25 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of
30 ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the
35 trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

Additional Adjunct Ingredients

A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium

salts such as MgCl_2 , MgSO_4 , and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C_{13-15} ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

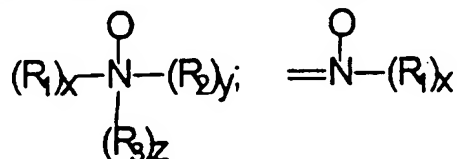
Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 10.5. Liquid dishwashing product formulations preferably have a pH between about 6.8 and about 9.0. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Dye Transfer Inhibiting Agents - The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers suitable for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $pK_a < 10$, preferably $pK_a < 7$, more preferred $pK_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful as dye transfer inhibiting polymers in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which has an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also suitable for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a

molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention also may employ as a dye transfer inhibitor a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP dye transfer inhibitors can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

Enzymes - Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application

Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al. published January 9, 1985).

Amylases include, for example, -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

5 The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al. issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine
10 mollusk (*Dolabella Auricula Solander*). suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME (Novo) is especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on
15 February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The
20 Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent
25 transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

30 A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868,
35 Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405,

Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

Enzyme Stabilizers - The enzymes employed herein are stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. 4,537,706. Typical detergents, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from about 0.05% to about 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

Bleaching Compounds - Bleaching Agents and Bleach Activators - The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from
5 about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent
10 compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include
15 magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983.
20 Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium
pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g.,
25 OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated
30 with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the
35 washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine

(TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

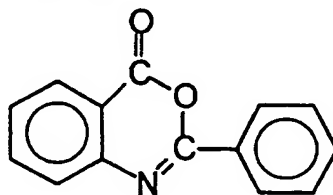
Highly preferred amido-derived bleach activators are those of the formulae:



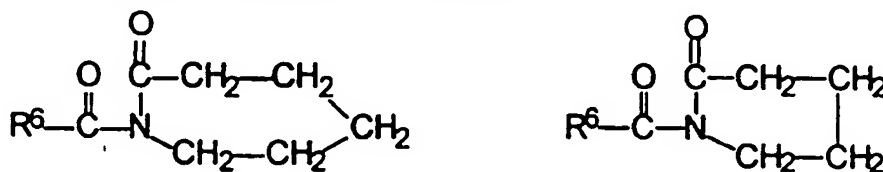
5 wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms. R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

10 Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by
15 Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



20 wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl
25 valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated
30 bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent

4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound.

5 Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-}$
 10 $\text{triazacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_3(\text{OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779;
 15 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry
 20 liquor.

Polymeric Soil Release Agent - Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of
 25 hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents
 30 having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30
 35 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface.

said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C₃ oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C₃ oxyalkylene terephthalate units is about 2:1 or lower, (ii) C₄-C₆ alkylene or oxy C₄-C₆ alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate, having a degree of polymerization of at least 2, or (iv) C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C₁-C₄ alkyl ether and/or C₄ hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C₄-C₆ alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as MO₃S(CH₂)_nOCH₂CH₂O-, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C₁-C₄ alkyl and C₄ hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material
5 ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are
10 described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

15 Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably, from
20 about 0.2% to about 3.0%.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5
25 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

30

PROCESS

Included in the present invention is a process for making a structured detergent composition consisting essentially of the surfactant and the hydrophilic, finely-divided silica. The process comprises the step of mixing an paste of the surfactant with the finely divided hydrophilic silica, under
35 adequate mixing to intimately combine the components into an homogeneous mixture. The silica is well-dispersed in the structured detergent composition. The resultant detergent composition has a hardened or firmer physical structure than the detergent surfactant.

Also included in the present invention is a process for making a structured surfactant composition for a detergent composition comprising the steps of:

- 5 a) Mixing from about 1% to about 20% of a hydrophilic, finely-divided particulate silica and from about 35% to about 60% of a detergent surfactant, thereby forming a hardened paste;
- b) Applying shear force to the hardened paste to form a flowable liquid; and
- 10 c) Dispersing the flowable liquid into fine droplets and agglomerating with dry detergent powder comprising other detergent adjuvants selected from the group consisting of other detergent surfactant, detergent builders, silica, and mixtures thereof, to form particles using a high speed mixer.

The silica particulate is preferably a hydrophilic precipitated silica and the detergent surfactant paste is an anionic surfactant, most preferably alkylalkoxy sulfate comprising an alkyl
15 portion of from 6 to 18 carbon atoms and an alkoxy portion comprising, an average, from about 0.5 to about 20 moles of alkoxy, preferably ethoxy, units, more preferably from about 0.5 to about 5 ethoxy units.

In order to make the structured surfactant composition, any suitable apparatus capable of
20 handling viscous paste is required. Suitable apparatus includes, for example, twin-screw extruders, Teledyne compounders, etc.

In order to make a detergent composition comprising the structured surfactant composition, suitable apparatus includes, for example, mixers/agglomerators can be used. In one preferred embodiment, the
25 process of the invention is continuously carried out.

The process preferably further comprises another step wherein the granulated surfactant composition is dusted with silica or zeolite.

30

EXAMPLES

Example 1

The structured surfactant composition can be made in the following way: the hydrophilic silica particulate is mixed with an alkylethoxy sulfate paste in a single-screw or twin-screw extruder. The pre-mix of soda ash, builder, zeolite and precipitated silica is agglomerated with the structured
35 surfactant composition in a plowshare mixer. The resulting particle has a density of 600 to 800 g/l.

Example 2

| | | |
|----|-------------------------------------|---------|
| | Ingredient | % |
| | CFAS | 21 |
| | CFA | 1 |
| | AE45-T | 0.8 |
| 5 | Structured Surfactant Composition * | 3.3 |
| | of Example 1 | |
| | STPP | 22.5 |
| | Zeolite | 12.6 |
| | Polymer | 0.7 |
| 10 | Other detergent adjuvants | Balance |

*Structured surfactant composition is comprised of AE3S at 70%, Hydrophilic precipitated silica at 2% and water at 28%.

15 Example 3

| | | |
|----|------------------------------------|---------|
| | Ingredient | % |
| | LAS | 20.7 |
| | STPP | 22.7 |
| | Carbonate | 22 |
| 20 | Zeolite | 14 |
| | Structured surfactant Composition* | 3.3 |
| | of Example 1 | |
| | Other detergent adjuvants | Balance |

25 *Structured surfactant composition is comprised of AE3S at 70%, Hydrophilic precipitated silica at 2% and water at 28%.

Example 4

| | | |
|----|--------------------------------|---------|
| | Ingredient | % |
| 30 | LAS | 24.5 |
| | STPP | 17.9 |
| | Soda Ash | 30 |
| | Zeolite | 11.9 |
| | Surfactant Composition (AE3S)* | 3.3 |
| 35 | of Example 1 | |
| | Other detergent adjuvants | Balance |

*Structured surfactant composition is comprised of AE3S at 70%, Hydrophilic precipitated silica at 2% and water at 28%.

What is claimed is:

1. A structured surfactant composition consisting essentially of:
 - (a) from about 35% to about 60% of a detergent surfactant;
 - (b) from about 1% to about 20% of hydrophilic, finely-divided silica particulate; and
 - (c) from about 15% to about 25% moisture.
- 5 2. A surfactant composition according to Claim 1, wherein the detergent surfactant is selected from the group consisting of anionic, cationic, zwitterionic, ampholytic surfactants and mixtures thereof.
3. A surfactant composition according to Claim 2, wherein the silica particulate is hydrophilic precipitated silica.
4. A surfactant composition according to Claim 3, wherein the detergent surfactant is alkyl ether sulfate of the formula $R-E_nSO_3M$, wherein:
 - (i) R is C8-20 alkyl chain;
 - (ii) E is an ethoxy unit;
 - 5 (iii) n is from 1-20; and
 - (iv) M is a cation.
5. A granular detergent composition comprising:

from about 2% to about 70% of a structured surfactant composition, the surfactant composition consisting essentially of:

 - (i) from about 35% to about 60% of a detergent surfactant;
 - 5 (ii) from about 1% to about 20% of hydrophilic, finely-divided silica particulate; and
 - (iii) from about 15% to about 25% moisture; and
 - (b) from about 30% to about 98% other detergent adjuvants selected from the group consisting of other detergent surfactants, detergent builders, silica, and mixtures thereof.
- 10 6. A composition according to Claim 5, wherein the detergent surfactant in (a)(i) is anionic surfactant and the silica particulate in (a)(ii) is hydrophilic precipitated silica.
7. A composition according to Claim 6, wherein the anionic surfactant is an alkyl ether sulfate of the formula $R-E_n-SO_3M$, wherein:
 - (a) R is C12-18, alkyl chain;

- 5 (b) E is an ethoxy unit;
(c) n is from 1-20; and
(d) M is a cation.

8. A process for making a surfactant composition for a detergent composition comprising the steps of:

- 5 a) mixing from about 1% to about 20% of a hydrophilic, finely-divided particulate silica, from about 35% to about 60% of a detergent surfactant, and from about 15% to about 25% moisture, thereby forming a hardened paste;
b) Applying shear force to the hardened paste to form a flowable liquid; and
c) Dispersing the flowable liquid into fine droplets and agglomerating with dry detergent powder comprising other detergent adjuvants selected from the group consisting of other detergent surfactant, detergent builders, silica, and mixtures thereof, to form
10 particles.using a high speed mixer.

9. A process according to Claim 8, wherein the silica particulate is a hydrophilic precipitated silica and the detergent surfactant is an anionic surfactant paste.

10. A process for making a granular detergent composition comprising the steps of:

- 5 a) mixing from about 1% to about 20% of a hydrophilic, finely-divided particulate silica, from about 15% to about 25% moisture, and from about 35% to about 60% of an alkyl ether sulfate surfactant of the formula $R-E_n-SO_3M$, wherein:
R is C12-15, alkyl chain;
E is an ethoxy unit;
n is 3; and
M is a sodium ion,
thereby forming a structured surfactant composition; and
10 b) granulating the surfactant composition upon mixing with a dry detergent powder comprising other detergent adjuvants selected from the group consisting of other detergent surfactant, detergent builders, silica, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/13448

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 1/29, 3/14, 3/39

US CL : 510/466, 444,493,537

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/466, 444,493,537

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| Y | US, A, 4,925,585 (STRAUSS ET AL.) 15 May 1990, See col. 2, lines 15-20, 29-33, 50-54, col. 3, lines 1-10, col. 4, lines 28-40, col. 5, lines 29-33, | 1-10 |
| Y | US, A, 5,045,225 (ARONSON ET AL) 03 September 1991, see col. 4, lines 17-18, col. 7, lines 18-46, col. 8, lines 1-23, Table 9. | 1-7 |
| P,Y | US, A, 5,529,722 (AOUAD ET AL.) 25 June 1996, see col. 2, lines 18-45, col. 3, line 65- col. 4, line 30, col. 5, line 1 - col. 7, line 10. | 1-10 |
| Y | US, A, 4,726,908 (KRUSE ET AL.) 23 February 23, 1988, See col. 3, lines 18-55, col. 5, lines 1-35. | 1-10 |



Further documents are listed in the continuation of Box C.



See patent family annex.

| | | |
|--|-----|--|
| * Special categories of cited documents: | * T | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| * A | | document defining the general state of the art which is not considered to be of particular relevance |
| * E | | earlier document published on or after the international filing date |
| * L | | document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) |
| * O | | document referring to an oral disclosure, use, exhibition or other means |
| * P | | document published prior to the international filing date but later than the priority date claimed |
| | * X | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| | * Y | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| | * Z | document member of the same patent family |

Date of the actual completion of the international search

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17 JAN 1997

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/13448

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS

Search terms: hydrophilic silica, moisture, water, structured surfactant#, sipernat, surfactant paste#, flowable liquid, ethoxy sulfate#